

FORM PCT 1390
REV. 5/93

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NO.
EBERLE ET AL - 4 (PCT)

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

10/030614

INTERNATIONAL APPLICATION NO.
PCT/EP 00/05519

INTERNATIONAL FILING DATE
JUNE 15, 2000

PRIORITY DATE CLAIMED
JULY 8, 1999

TITLE OF INVENTION **PROCESS FOR PRODUCING MONOLITHIC OXIDATION CATALYSTS AND THEIR
USE IN THE GAS-PHASE OXIDATION OF HYDROCARBONS**

APPLICANT(S) FOR DO/EO/US **HANS-JÜRGEN EBERLE, OLAF HELMER, KARL-HEINZ STOCKSIEFEN, DR.
STEFAN TRINKHAUS, ULRICH WECKER, NORBERT ZEITLER**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

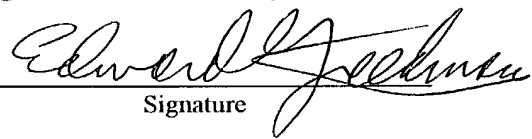
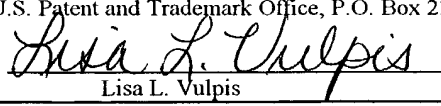
1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371 (f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau)
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has **NOT** expired.
 - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

PCT/ISA/210 - Int'l. Search Report (English)

Applicant Claims Priority under 35 U.S.C. §119 of Germany (country) Application No. 199 31 902.2 filed July 8, 1999.
Applicant Claims Priority under 35 U.S.C. §120 of: PCT No. PCT/EP00/05519, filed June 15, 2000.

APPLICATION NO. (if known, see 37 CFR 1.5)				INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NO.
10/030614				PCT/EP 00/05519	EBERLE ET AL-4-PCT
<input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)):					
Search Report has been prepared by the EPO or JPO.....\$890.00					
International preliminary examination fee paid to USPTO (37 CFR 1.482).....\$690.00					
Neither international preliminary examination fee paid (37 CFR 1.82) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO.....\$1,040.00					
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4).....\$100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$ 890.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than ____ 20 ____ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).					
Claims	Number Filed	Number Extra	Rate		
Total Claims	21 - 20 =	- 1 -	X \$18.00	\$ 18.00	
Independent Claims	2 - 3 =	- 0 -	X \$80.00	\$	
Multiple dependent claim(s) (if applicable)			+ \$270.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$ 908.00	
Reduction by 1/2 for Small Entity status.				\$	
SUBTOTAL =				\$ 908.00	
Processing fee of \$130.00 for furnishing the English translation later than ____ 20 ____ 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$ 908.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)) The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
TOTAL FEES ENCLOSED =				\$ 908.00	
				Amount to be:	
				refunded	\$
				charged	\$
<input type="checkbox"/> Applicant claims Small Entity status.					
a. <input checked="" type="checkbox"/> A check in the amount of \$ 908.00 to cover the above fees is enclosed.					
b. <input type="checkbox"/> Please charge my Deposit Account No. 03-2468 in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.					
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment, to Deposit Account No. 03-2468. A duplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: COLLARD & ROE, P.C. 1077 Northern Boulevard Roslyn, New York 11576-1696 (516) 365-9802					
 Signature					
Edward R. Freedman Reg. No. 26,048					
Express Mail No. EL 871451155 US Date of Deposit January 3, 2002					
I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, on the date indicated above, and is addressed to the Box PCT, U.S. Patent and Trademark Office, P.O. Box 2327, Arlington, VA 22202.					
 Lisa L. Vulpis					

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531 Rec'd PCT/FTC 03 JAN 2002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: EBERLE ET AL - 4 (PCT)
PCT No.: PCT/EP '00/05519 FILED: JUNE 15, 2000
TITLE: PROCESS FOR PRODUCING MONOLITHIC OXIDATION
CATALYSTS AND THEIR USE IN THE GAS-PHASE OXIDATION
OF HYDROCARBONS

PRELIMINARY AMENDMENT

BOX PCT
U.S.P.T.O.
P.O. Box 2327
Arlington, VA 22202

Dear Sir:

Preliminary to Examination, please amend the above-
identified application as follows:

IN THE ABSTRACT

Please insert the Abstract attached hereto on its own
separate page.

IN THE SPECIFICATION

On Page 1, below the title, and above line 5, please insert
as follows:

--CROSS REFERENCE TO RELATED APPLICATIONS

Applicant claims priority under 35 U.S.C. §119 of German Application No. 199 31 902.2 filed July 8, 1999. Applicant also claims priority under 35 U.S.C. §120 of PCT/EP00/05519 filed June 15, 2000. The international application under PCT article 21(2) was not published in English.

BACKGROUND OF THE INVENTION

1. Field of the Invention--

On Page 1, between lines 7 and 8, please insert:

--2. The Prior Art--

On page 4, between lines 6 and 23, please cancel the following paragraph:

"AT-A 9201926 describes a process for preparing phthalic anhydride in a main reactor having a downstream adiabatic reaction zone. Here, it is expressly stated that, for economic reasons, it is advantageous for the adiabatic reactor to be connected directly to the main reactor. Apart from the use of catalyst base bodies in the form of rings or spheres, mention is also made of the possible use of a catalyst having a monolithic structure, for example in the form of a honeycomb. In the reaction procedure described, this measure enables the yield of phthalic anhydride to be increased by about 1% by weight. The

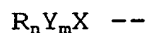
formation of the by-product phthalide is at the same time significantly reduce. The use of the monolithic catalyst shape mentioned is not described in any example. Likewise, no details are given of the production of a monolithic catalyst and associated problems."

On page 5, between lines 21 and 22, please insert:

--SUMMARY OF THE INVENTION--

On Page 5, please cancel the last paragraph in lines 30 to 36, and please replace by inserting the following paragraph:

--The invention provides a process for producing monolithic supported catalysts for gas-phase oxidation by coating the catalyst support by means of a suspension, wherein the latter comprises catalytically active composition comprising one or more types of TiO_2 and 1-10% by weight of one or more surfactants of the formula



On page 10, between lines 17 and 18, please insert:

--DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS--

A Marked-Up Version of Pages 1, 4, 5, and 10 is enclosed.

IN THE CLAIMS:

Please cancel claims 1 to 22 without prejudice, and please replace by inserting new claims 23 to 43 to as follows:

23. A process for producing monolithic supported catalysts for gas-phase oxidation comprising

coating a catalyst support with a suspension,

wherein the suspension comprises catalytically active composition comprising at least one type of TiO_2 and 1-10% by weight of at least one surfactant of the formula



where R is a hydrophobic group of the surfactant and n is 1, 2 or 3; Y is a hydrophilic group of the surfactant and m is 0, 1, 2 or 3, and X is a hydrophilic head group of the surfactant; and the percent by weight is based upon the total weight of the composition.

24. The process as claimed in claim 23,

wherein the surfactant comprises from 2 to 5% by weight based upon the total weight.

25. The process as claimed in claim 23,

wherein the head group X present in the surfactant is a functional group selected from the group consisting of

carboxylate, polycarboxylate, phosphate, phosphonate, sulfate and sulfonate.

26. The process as claimed in claim 25,
wherein at least one of the functional groups of the head group X is selected from the group consisting of free acid group, ammonium salt, and alkaline earth metal salt.

27. The process as claimed in claim 23,
wherein the hydrophilic group Y is bound to a central atom of the head group X either directly or via an oxygen.

28. The process as claimed in claim 23,
wherein the hydrophobic group R of the surfactant used is bound to the head group X via a hydrophilic group Y.

29. The process as claimed in claim 23,
wherein hydrophobic groups R of the surfactant used are selected from the group consisting of saturated alkyl radicals with carbon building blocks having from 5 to 30 carbon atoms, unsaturated alkyl radicals with carbon building blocks having from 5 to 30 carbon atoms; and
branched alkyl radicals with carbon building blocks having from 5 to 30 carbon atoms and are bound either directly or

via aryl groups to a group selected from the group consisting of the hydrophilic group Y and the head group X.

30. The process as claimed in claim 23,
wherein the hydrophilic group Y of the surfactants used comprises polymeric alkoxy units whose degree of polymerization is from 1 to 50 monomer units.

31. The process as claimed in claim 23,
wherein said at least one surfactant is selected from the group consisting of calcium alkylarylsulfonate, alkylphenol ethoxylate, ammonium alkylarylsulfonate, calcium dodecylbenzenesulfonate, polyethoxy (dinonyl phenyl ether phosphate), polyoxoethylene (lauryl ether phosphate), polyethoxy (tridecyl ether phosphate), calcium dodecylbenzenesulfonate, tridecyl phosphate ester, ethoxylated phosphated alcohol, alkyl polyoxyethylene ether phosphate, and ammonium nonyl phenyl ether sulfate.

32. The process as claimed in claim 23,
wherein the catalytically active composition further comprises V_2O_5 as an additional component.

33. The process as claimed in claim 23,

wherein the catalytically active composition comprises promoters.

34. The process as claimed in claim 23,
wherein the catalyst support used is at least one material selected from the group consisting of cordierite, silicate, silicon dioxide, silicon carbide, aluminum oxide, aluminate, metal and metal alloy.

35. The process as claimed in claim 23,
wherein a catalyst support body used is selected from the group consisting of a honeycomb, a support having open cross-channel structure, a support having closed cross channel structure, and mixtures thereof.

36. The process as claimed in claim 35, wherein
wherein the catalyst support body used is a honeycomb having a cell density of a number of channels, of from 100 to 400 csi (cells per square inch).

37. A method for preparing phthalic anhydride comprising
a gas-phase oxidation reaction of o-xylene by contacting said o-xylene with a monolithic supported catalyst obtainable by the process as claimed in claim 23 in an adiabatic reactor in combination with an isothermally operated reactor.

38. A method for preparing phthalic anhydride comprising a gas-phase oxidation reaction of naphthalene by contacting said naphthalene with a monolithic supported catalyst obtainable by the process as claimed in claim 23 in an adiabatic reactor in combination with an isothermally operated reactor.

39. A method for preparing phthalic anhydride comprising a gas-phase oxidation reaction of a mixture of o-xylene and naphthalene by contacting said mixture of o-xylene and naphthalene with a monolithic supported catalyst obtainable by the process as claimed in claim 23 in an adiabatic reactor in combination with an isothermally operated reactor.

40. The method as claimed in claim 37, wherein the adiabatic reactor has upstream gas cooling in combination with an isothermally operated reactor.

41. The method as claimed in claim 37, wherein the adiabatic reactor has upstream gas cooling, where gas cooling and the reaction are carried out in a joint apparatus, in combination with an isothermally operated reactor.

42. The method as claimed in claim 37,

wherein the adiabatic reactor has upstream gas cooling and downstream gas cooling, where gas cooling and the reaction are carried out in a joint apparatus, in combination with an isothermally operated reactor.

43. A catalyst comprising

a catalyst support coated with a suspension; and said suspension comprises a catalytically active composition comprising

at least one type of TiO_2 and 1-10% by weight of at least one surfactant of the formula



where R is a hydrophobic group of the surfactant and n is 1, 2 or 3; Y is a hydrophilic group of the surfactant and m is 0, 1, 2 or 3, and X is a hydrophilic head group of the surfactant; and

the percent by weight is based upon the total composition weight.

REMARKS

By this Preliminary Amendment, the Specification has been amended to include a cross-reference to related applications which has been inserted in page 1. Also pages 1, 5, and 10 have been amended to recite the Specification section headings required by U.S. practice. In addition, pages 4 and 5 of the U.S. Specification have been amended to conform to the changes made in the International Office.

The amendments to the claims are to cancel the originally filed claims 1 to 22 without prejudice, and to replace these claims with new claims 23 to 43. New claims 23 to 43 eliminate the multiple dependency of the claims, so as to avoid the U.S.P.T.O. surcharge therefor. Also claims 23 to 43 have been written so as to comply with U.S. formal requirements. Claims 23 to 43 correspond to the amended claims filed in the International Office.

An Abstract of the Disclosure on its own separate page is enclosed.

No new matter has been introduced by this amendment. Entry of this amendment is respectfully requested.

Respectfully submitted,

EBERLE ET AL - 4 (PCT)

By:

Edward R. Freedman
Allison C. Collard, Reg. No. 22,532
Edward R. Freedman, Reg. No. 26,048
Attorneys for Applicant

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1077 Northern Boulevard
Roslyn, New York 11576
(516) 365-9802

ERF/mt

Enclosure: (1) Abstract of the Disclosure;
(2) Marked-Up Version of Amended Specification pages
1, 4, 5 and 10;

EXPRESS MAIL # EL 871 451 155 US
DATE: January 3, 2002

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10, on the date indicated above, and is addressed to the U.S. Patent and Trademark Office, Box PCT, P.O. Box 2327, Arlington, VA 22202.

Lisa L. Vulpis

Lisa L. Vulpis

ABSTRACT OF THE DISCLOSURE

A method is for producing monolithic substrate catalysts and for their use in the gas phase oxidation of hydrocarbons. The catalysts are obtained by coating the catalyst substrate with a suspension that includes a catalytically active compound and one or more surfactants of the general formula R_nY_mX . R represents the hydrophobic part of the surfactant, with n being 1, 2 or 3. Y represents the hydrophilic part of the surfactant, with m being 0, 1, 2 or 3 and X represents the hydrophilic head group of the surfactant.

**Process for producing monolithic oxidation catalysts
and their use in the gas-phase oxidation of
hydrocarbons**

5 The invention relates to a process for
producing monolithic oxidation catalysts and to their
use in the gas-phase oxidation of hydrocarbons.

 Supported catalysts for the gas-phase oxidation
of hydrocarbons to give the corresponding oxidation
10 products such as carboxylic acids, carboxylic
anhydrides or aldehydes, which catalysts have a
catalytically active surface coating consisting
essentially of titanium dioxide (TiO_2) and divanadium
pentoxide (V_2O_5), have been known for a long time. A
15 typical example of the use of such catalysts is the
preparation of phthalic anhydride, in which mixtures of
o-xylene and air or naphthalene and air or o-xylene,
naphthalene and air are passed over an appropriate
catalyst in a shell-and-tube reactor. The heat
20 generated in this strongly exothermic reaction is
customarily removed (cooling, isothermal reaction
conditions) by means of a salt melt which surrounds the
reaction tubes.

 The supported catalysts used here comprise an
25 inert support body, for example having a ring shape or
a spherical shape, on which the actual catalytically
active composition is present. The active composition
consists predominantly of the main components TiO_2 in
the anatase form and V_2O_5 . To improve the control of the
30 activity and to improve the selectivity, further
activating or deactivating additives, for example
oxides of transition elements or alkali metal
compounds, are frequently added in small amounts as
dopants (promoters) to the catalytically active
35 composition.

 The supported catalysts are generally produced
by spraying aqueous suspensions or aqueous solutions of
 TiO_2 and V_2O_5 , frequently with addition of promoters and

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possibly binders for improving adhesion of the active components to the support, onto the support bodies.

As support bodies, use is made of regularly shaped, mechanically stable bodies such as spheres, rings, half rings, saddles, etc., particularly preferably rings or spheres. The size of the support bodies is determined predominantly by the dimensions of the reactor, especially by the internal diameter of the reaction tubes.

Support materials used are, for example, steatite, Duranit, earthenware, silicon dioxide, silicon carbide, aluminates, metals and metal alloys.

EP-A 744214 (US-A 5792719) discloses a procedure for producing catalysts in which TiO_2 , V_2O_5 , SiC and possibly dopants such as CsCO_3 and $(\text{NH}_4)_2\text{HPO}_4$ are stirred in aqueous suspension for a number of hours, and the suspension is subsequently admixed with an organic binder. This suspension is sprayed onto the support material and the supported catalyst is dried.

In industry, it is customary for each of the reaction tubes to be filled with various catalysts which have different catalytically active compositions. These can be arranged, for example, in two superposed zones, an upper zone and a lower zone. This measure makes it possible to match the activity of the catalyst system in the reactor appropriately to the course of the reaction.

During the reaction, the major part of hydrocarbon is reacted in the upper part of the reaction tube. As a result, the highest temperatures inevitably also occur there. In the lower part of the tube, only a sort of after-reaction takes place. There, remaining o-xylene/naphthalene and intermediates, for example o-tolualdehyde and phthalide, are converted into phthalic anhydride. Furthermore, by-products such as quinones are also oxidized further.

As a result of aging processes, all catalysts lose activity as the time for which they have been used

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increases. This occurs predominantly in the main reaction zone, since this is where the catalyst is subject to the highest temperatures. During the life of the catalyst, the main reaction zone migrates ever further into the catalyst bed. This steadily decreases the length of the remaining catalyst bed and adversely affects the after-reaction. As a consequence, intermediates and by-products can no longer be reacted completely and the product quality of the phthalic anhydride produced therefore deteriorates to an increasing extent. An aging process is particularly critical in the case of high feed loadings. Although the fall-off in the reaction and thus the deterioration in product quality can be countered by increasing the reaction temperature, for example by means of the salt bath temperature, but only to a temperature of about 400°C, this temperature increase is always associated with a loss in yield.

DE-A 1793267 (GB-A 1274471) describes a process for preparing phthalic anhydride, in which the overall oxidative reaction is divided in process engineering terms into two parts. The reaction is controlled so that the reaction conditions in the second part, known as the after-reaction, are significantly more aggressive than in the first part. This can be achieved, for example, by carrying out the after-reaction without cooling, i.e. adiabatically. This after-reaction can be carried out in a separate reactor having different tube dimensions or even in a downstream shaft oven.

DE-A 2005969 describes a process for preparing phthalic anhydride, in which from about 80 to 99% of the total feed is reacted isothermally, i.e. cooled, in the main reaction. Conversion of the remaining unreacted feed occurs in a downstream adiabatic reactor. In addition, in the reaction procedure described, the gas mixture leaving the isothermal reactor is cooled further before it enters the

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downstream adiabatic reactor. This process variant is likewise intended to enable the phthalic anhydride formed to be obtained largely free of by-products and without a loss in yield. Here too, a shaft oven is
5 claimed as adiabatic reactor.

AT-A 9201926 describes a process for preparing phthalic anhydride in a main reactor having a downstream adiabatic reaction zone. Here, it is expressly stated that, for economic reasons, it is
10 advantageous for the adiabatic reactor to be connected directly to the main reactor. Apart from the use of catalyst base bodies in the form of rings or spheres, mention is also made of the possible use of a catalyst having a monolithic structure, for example in the form
15 of a honeycomb. In the reaction procedure described, this measure enables the yield of phthalic anhydride to be increased by about 1% by weight. The formation of the by-product phthalide is at the same time significantly reduced. The use of the monolithic
20 catalyst shape mentioned is not described in any example. Likewise, no details are given of the production of a monolithic catalyst and associated problems.

Owing to the laminar flow occurring in
25 honeycomb catalysts, they have only a very low pressure drop even at very high gas velocities. However, a disadvantage is that, owing to the lack of turbulent flow resulting from the shape, heat and mass transfer in the honeycomb channels, and thus heat removal, are
30 greatly reduced. This situation makes use of honeycomb catalysts as catalyst supports virtually impossible for strongly exothermic processes in conjunction with a selective oxidation. Honeycomb catalysts have therefore become established industrially only in waste gas
35 purification or waste gas incineration where all the organic constituents undergo total oxidation to CO_2 .

Coating monolithic support material with a catalytically active composition comprising the main

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constituents TiO_2 , V_2O_5 and possibly dopants by generally known methods, for example a dipping process, is found to be impractical. This is because coating suspensions based on commercially available TiO_2 have a
5 very high viscosity even at solids concentrations of 30-35% by weight and thus make coating of the channels of a monolithic support material virtually impossible without blocking the channels.

In order to coat monolithic catalyst supports
10 with the necessary amount of catalytically active composition, for example 50-150 g of active composition per liter of catalyst, the coating process would have to be carried out with such a low-concentration "active composition" suspension that the necessary layer
15 thickness would be achieved only after repeating the coating process a number of times. However, this at the same time once again increases the problem of blocking of the channels in the catalyst support because of the multiple coating steps. Furthermore, this is associated
20 with significantly more work and thus with increased costs and is therefore uneconomical.

It is therefore an object of the invention to provide a simple and preferably single-stage process for producing monolithic catalysts based on TiO_2 /metal
25 oxides.

It has now surprisingly been found that the viscosity of highly concentrated TiO_2 coating suspensions having a high solids content can be greatly reduced by addition of surfactants.

30 The invention provides a process for producing monolithic supported catalysts for gas-phase oxidation by coating the catalyst support by means of a suspension, wherein the latter comprises catalytically active composition and one or more surfactants of the
35 formula



5 The viscosity of highly concentrated TiO_2 coating suspensions having a solids content of greater than 30% by weight can be greatly reduced by addition of from 1 to 10% by weight, preferably from 2 to 5% by weight, of surfactants of the formula $\text{R}_n\text{Y}_m\text{X}$.

Preference is given to surfactants having head groups X selected from among phosphates, phosphonates, sulfates, sulfonates and carboxylates, dicarboxylates (malonic acid derivatives, succinic acid derivatives, adipic acid derivatives, maleic acid derivatives, phthalic acid derivatives) and polycarboxylates, for example polyacrylates, polymethacrylates or polymaleic acid derivatives substituted by surfactant radicals (R,Y).

30 The hydrophilic group Y can be bound to the
central atom of the head group X either directly or via
an oxygen. Preferred central atoms are carbon,
phosphorus and sulfur.

Preferred embodiments of the hydrophobic parts R are alkyl radicals having relatively long-chain carbon building blocks with from 5 to 30 carbon atoms,

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preferably from 10 to 20 carbon atoms. The alkyl radicals can be saturated or unsaturated or branched carbon chains. The alkyl radicals can be bound directly or via aryl groups to the hydrophilic part Y or the head group X.

The hydrophilic radical Y generally comprises polymeric alkoxy units, preferably propoxy, ethoxy or methoxy units, with the degree of polymerization being able to be from 1 to 50 monomer units, preferably from 5 to 20 monomer units.

The coating suspension used according to the invention can comprise, for example, surfactants of the formula R_nY_mX selected from the group consisting of calcium alkylarylsulfonates, ammonium alkylaryl-sulfonates, calcium dodecylbenzenesulfonate, polyethoxy(dinonyl phenyl ether phosphate), polyoxoethylene(lauryl ether phosphate), polyethoxy-(tridecyl ether phosphate), calcium dodecylbenzenesulfonate, tridecyl phosphate esters, ethoxylated phosphated alcohols, alkyl polyoxyethylene ether phosphate, ammonium nonyl phenyl ether sulfate.

The surfactants can be used without addition of further surfactants or together with other surfactants, for example alkylphenol ethoxylate.

The addition according to the invention of the surfactants to the coating suspension allows low-viscosity coating suspensions having high solids contents of TiO_2 and/or V_2O_5 to be prepared and to be used for coating monolithic support material, for example honeycombs and supports having open or closed cross-channel structures. The coating suspensions may further comprise other additives, for example SiC. The solids contents of catalytically active composition in such suspensions can be set to values of up to 50% by weight and above. Such highly concentrated suspensions allow monolithic and, in particular, honeycomb catalyst supports coated with from 50 to 150 g of active

Suspensions having a solids content of TiO_2 of greater than 35% by weight have, owing to the high viscosity, greatly reduced flow and can therefore no longer flow through narrow channels. Changing to larger particle sizes does not lead to success either. The addition of one or more of the surfactants claimed significantly improves flow.

15 The coating of honeycombs with coating
suspensions without addition of surfactants can be
carried out without problems only using suspensions
having a relatively low solids content of about 30% by
weight. However, the amounts of active composition
20 which can be applied in this way are only about 20 g/l
of catalyst. If the solids content is slightly
increased, the viscosity of the suspension increases so
much that the suspension can no longer flow out of the
honeycomb channels and blocking of the channels
25 therefore results.

30 Applied amounts of over 100 g of solid/l of honeycomb catalyst can be achieved without problems in one coating step when using the surfactants claimed.

Examples of support materials suitable for coating by the process of the invention are materials such as cordierite, silicates, silicon dioxide, silicon carbide, aluminum oxide, aluminates or mixtures of these materials and metals or metal alloys. The support bodies can also have closed or open cross-channel

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structures. The suspensions used according to the invention enable honeycombs having a high to very high cell density to be coated without the danger of blocking the channels.

- 5 Preference is given to honeycombs having a cell density, i.e. a number of channels, of from 100 to 400 csi (cells per square inch), particularly preferably from 100 to 200 csi.

10 Monolithic catalysts are very well suited to the selective oxidation of o-xylene/air mixtures having low o-xylene contents to give PA. The monolithic catalysts do not in any event have a tendency to produce a runaway reaction. Surprisingly, the monolithic catalysts are superior to the conventional
15 ring catalyst (for the same active composition).

Catalysts produced according to the invention and having a content of active composition of from 40 to 200 g per liter of catalyst are particularly advantageous. At a comparable temperature, these
20 achieve higher conversions, better PA selectivities and smaller amounts of by-products.

The honeycomb catalysts produced according to the invention are very useful as catalysts for an after-reaction of a PA process gas comprising one or
25 more of the starting materials o-xylene and naphthalene and/or intermediates such as tolualdehyde, phthalide, naphthoquinone, etc. This reaction is advantageously carried out at lower gas inlet temperatures, based on the temperature of the main reactor. In this after-
30 reaction, a major part of the underoxidation products can be removed from the reaction gas and reacted further to form PA. Surprisingly, this also occurs at relatively high space velocities of 20,000-30,000 h⁻¹. Even in the presence of relatively high contents of
35 underoxidation products together with a high concentration of PA, no runaway reaction occurs when using the catalysts of the invention.

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The monolithic catalysts produced according to the invention are particularly suitable for preparing phthalic anhydride in an adiabatic reactor (after-reactor) in combination with an isothermally operated reactor (main reactor, for example filled with a bed of particulate catalyst).

The adiabatic reactor can also be operated advantageously with upstream gas cooling. In a particularly preferred embodiment, the upstream gas cooling and the adiabatic reaction are carried out in a joint apparatus.

In industry, it is customary to cool the reaction gas in a gas cooler before isolation of the product. The upstream gas cooling, the adiabatic reaction in the monolithic catalyst bed and further cooling can be carried out within the reactor or outside the reactor, or in a joint apparatus.

The invention is illustrated in more detail by the following examples.

The following examples demonstrate the influence of surfactants from the group consisting of phosphoric esters on the viscosity of support oxide suspensions. The flow behavior of the suspensions prepared was determined by a method based on DIN 53211 using a flow cup. Two types of TiO_2 which differed from one another only in the particle size were tested. The mean particle diameter was 0.1 and 0.4 μm , respectively. This measurement method was selected since it could appropriately simulate flow of a suspension out of the honeycomb channels. As outflow nozzle, use was made of a nozzle having a diameter of 2 mm corresponding to a flow orifice area of 3.14 mm^2 . For comparison, a 200 csi honeycomb has a channel cross section of 2.3 mm^2 and a 100 csi honeycomb has a channel cross section of 4.66 mm^2 . If the viscosity of the suspension was too high, i.e. the suspension could not flow through the nozzle under these conditions, the experiment was repeated using a nozzle opening of 4 mm

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diameter. If no outflow of the suspension could be measured even under the altered conditions, the experiment was evaluated as "not measurable".

5 **Comparative Example 1 (30% strength by weight suspension without surfactant):**

A suspension was prepared from a mixture of 30 g of TiO_2 having a mean particle diameter of $0.1 \mu\text{m}$ and 70 g of water and was stirred for 2 hours. The flow
10 was subsequently measured in the flow cup. At a nozzle diameter of 2 mm, the outflow rate was 1.4 ml/sec.

Comparative Example 2 (33% strength by weight suspension without surfactant):

15 A suspension was prepared from a mixture of 33 g of TiO_2 having a mean particle diameter of $0.1 \mu\text{m}$ and 67 g of water and was stirred for 2 hours. The flow was subsequently measured in the flow cup. At a nozzle diameter of 2 mm, no outflow was observed. At a nozzle
20 diameter of 4 mm, the outflow rate was 6.2 ml/sec.

Comparative Example 3 (22% strength by weight suspension without surfactant):

A suspension was prepared from a mixture of
25 22 g of TiO_2 having a mean particle diameter of $0.4 \mu\text{m}$ and 78 g of water and was stirred for 2 hours. The flow was subsequently measured in the flow cup. At a nozzle diameter of 2 mm, the outflow rate was 1.7 ml/sec.

30 **Comparative Example 4 (25% strength by weight suspension without surfactant):**

A suspension was prepared from a mixture of
25 g of TiO_2 having a mean particle diameter of $0.4 \mu\text{m}$ and 75 g of water and was stirred for 2 hours. The flow
35 was subsequently measured in the flow cup. At a nozzle diameter of 2 mm, no outflow was observed. At a nozzle diameter of 4 mm, the outflow rate was 8.3 ml/sec.

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Example 5 (45% strength by weight suspension):

A suspension was prepared from a mixture of 45 g of TiO_2 having a mean particle diameter of $0.1 \mu\text{m}$, 55 g of water and 3.5 g of alkyl($\text{C}_8\text{-C}_{10}$)polyoxyethylene ether phosphate and was stirred for 2 hours. The flow was subsequently measured in the flow cup. At a nozzle diameter of 2 mm, the outflow rate was 0.9 ml/sec.

Example 6 (45% strength by weight suspension):

A suspension was prepared from a mixture of 45 g of TiO_2 having a mean particle diameter of $0.4 \mu\text{m}$, 55 g of water and 3.0 g of alkyl($\text{C}_8\text{-C}_{10}$)polyoxyethylene ether phosphate and was stirred for 2 hours. The flow was subsequently measured in the flow cup. At a nozzle diameter of 2 mm, the outflow rate was 2.0 ml/sec.

Example 7 (45% strength by weight suspension):

A suspension was prepared from a mixture of 45 g of TiO_2 having a mean particle diameter of $0.4 \mu\text{m}$, 55 g of water and 5.0 g of polyethoxydinonylphenyl ether phosphate and was stirred for 2 hours. The flow was subsequently measured in the flow cup. At a nozzle diameter of 2 mm, the outflow rate was 1.2 ml/sec.

Example 8 (45% strength by weight suspension):

A suspension was prepared from a mixture of 45 g of TiO_2 having a mean particle diameter of $0.4 \mu\text{m}$, 55 g of water and 2.0 g of a mixture of alkylphenol ethoxylate/calcium alkylarylsulfonate and was stirred for 2 hours. The flow was subsequently measured in the flow cup. At a nozzle diameter of 2 mm, the outflow rate was 1.3 ml/sec.

Example 9 (45% strength by weight suspension):

A suspension was prepared from a mixture of 45 g of TiO_2 having a mean particle diameter of $0.1 \mu\text{m}$, 55 g of water and 5.0 g of calcium dodecylbenzenesulfonate and was stirred for 2 hours. The flow was

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subsequently measured in the flow cup. At a nozzle diameter of 2 mm, the outflow rate was 0.5 ml/sec.

Example 10 (45% strength by weight suspension):

5 A suspension was prepared from a mixture of
45 g of TiO_2 having a mean particle diameter of $0.4 \mu\text{m}$,
55 g of water and 2.5 g of ammonium nonyl phenyl ether
sulfate and was stirred for 2 hours. The flow was
subsequently measured in the flow cup. At a nozzle
10 diameter of 2 mm, the outflow rate was 1.8 ml/sec.

Comparative Example 11:

 A suspension was prepared from a mixture of
38 g of TiO_2 having a mean particle diameter of $0.4 \mu\text{m}$,
15 9.5 g of V_2O_5 and 46.8 g of water and was stirred for
2 hours. The flow was subsequently measured in the flow
cup. The outflow rate could be measured neither using a
2 mm nozzle opening nor a 4 mm nozzle opening, since
the viscosity of the suspension was too high in both
20 cases.

Example 12:

 A suspension was prepared from a mixture of
38 g of TiO_2 having a mean particle diameter of $0.4 \mu\text{m}$,
25 9.5 g of V_2O_5 , 46.8 g of water and 3 g of
alkyl(C_8 - C_{10})polyoxyethylene ether phosphate and was
stirred for 2 hours. The flow was subsequently measured
in the flow cup. At a nozzle diameter of 2 mm, the
outflow rate was 1.3 ml/sec.

30 Examples 13 to 17 below demonstrate the
production of catalysts by way of coating experiments
on appropriate monolithic support bodies.

**Comparative Example 13 (without addition of
35 surfactant):**

 354 g of TiO_2 (BET about $30 \text{ m}^2/\text{g}$) having a mean
particle diameter of $0.1 \mu\text{m}$, 118 g of TiO_2
(BET $< 10 \text{ m}^2/\text{g}$) having a mean particle diameter of

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0.4 μm , 120 g of V_2O_5 and 8.24 g of $(\text{NH}_4)_2\text{HPO}_4$ were suspended in 1400 ml of deionized water and stirred for 18 hours to achieve homogeneous dispersion. The solids content of the suspension obtained was 29.6% by weight.

5 60 g of organic binder, namely a copolymer of vinyl acetate and vinyl laurate, in the form of a 50% strength by weight aqueous dispersion were then added. A monolithic ceramic support honeycomb made of cordierite and having a cell density of 200 cpsi and

10 dimensions of 7.5 cm \times 7.5 cm \times 15 cm was then dipped into this coating suspension and taken from the dipping bath after about 1 minute. The residues of suspension present in the channels were blown out using an air blower (at not more than 130°C). Complete drying of the

15 coated honeycomb was carried out in a drying oven at 130°C for 12 hours. The amount of active composition applied was 20 g/l of catalyst. The honeycomb was just able to be coated.

20 **Comparative Example 14 (without addition of surfactant):**

To produce a catalyst coated with a larger amount of active composition, 354 g of TiO_2 (BET about 30 cm^2/g) having a mean particle diameter of 0.1 μm ,

25 118 g of TiO_2 (BET < 10 m^2/g) having a mean particle diameter of 0.4 μm , 120 g of V_2O_5 and 8.24 g of $(\text{NH}_4)_2\text{HPO}_4$ were suspended in 1220 ml of deionized water and stirred for 18 hours to achieve homogeneous dispersion. The solids content of the suspension

30 obtained was 32.7% by weight. 60 g of organic binder, namely a copolymer of vinyl acetate and vinyl laurate, in the form of a 50% strength by weight aqueous dispersion were then added. Using this coating suspension, a monolithic ceramic support honeycomb made

35 of cordierite and having a cell density of 200 cpsi and dimensions of 7.5 cm \times 7.5 cm \times 15 cm was coated using a method analogous to Example 15. In this example, the suspension was so highly viscous that the channels

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could not be freed completely of excess suspension even with the aid of the blower. About 10% of the channels remained blocked. The coated honeycomb could not be used as a catalyst.

5

Comparative Example 15 (Coating of rings):

To produce a ring-shaped comparative catalyst, 73.7 g of TiO_2 (BET about $30 \text{ m}^2/\text{g}$) having a mean particle diameter of $0.1 \mu\text{m}$, 24.6 g of TiO_2 (BET $< 10 \text{ m}^2/\text{g}$) having a mean particle diameter of $0.4 \mu\text{m}$, 25 g of V_2O_5 and 1.7 g of $(\text{NH}_4)_2\text{HPO}_4$ were suspended in 400 ml of deionized water and stirred for 18 hours to achieve homogeneous dispersion. 6.2 g of organic binder, namely a copolymer of vinyl acetate and vinyl laurate, in the form of a 50% strength by weight aqueous dispersion were then added. All of this coating suspension was applied to 1225 g of steatite rings ($7 \times 7 \times 4 \text{ mm}$) as support material with evaporation of the water. The layer thickness of active composition was about $60 \mu\text{m}$.

Example 16 (Catalyst 1 according to the invention):

602 g of TiO_2 (BET about $30 \text{ m}^2/\text{g}$) having a mean particle diameter of $0.1 \mu\text{m}$, 200 g of TiO_2 (BET $< 10 \text{ m}^2/\text{g}$) having a mean particle diameter of $0.4 \mu\text{m}$, 204 g of V_2O_5 and 70 g of alkyl($\text{C}_8\text{-C}_{10}$)polyoxyethylene ether phosphate were suspended in 980 ml of deionized water and stirred for 18 hours to achieve homogeneous dispersion. The solids content of the suspension obtained was 51% by weight. 60 g of organic binder, namely a copolymer of vinyl acetate and vinyl laurate, in the form of a 50% strength by weight aqueous dispersion were then added. Using this coating suspension, a monolithic ceramic support honeycomb made of cordierite and having a cell density of 200 cpsi and dimensions of $7.5 \text{ cm} \times 7.5 \text{ cm} \times 15 \text{ cm}$ was coated using a method analogous to Example 15. Due to the viscosity-lowering

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action of the surfactant, the suspension not adhering to the wall flowed completely out of the channels without problems. Owing to the high solids content of the suspension used, 115 g of active composition per liter of catalyst could be applied in a single coating step. No channels of the honeycomb were blocked with active composition. The layer thickness of active composition was about 60 μm .

10 **Example 17 (Catalyst 2 according to the invention):**

602 g of TiO_2 (BET about 30 m^2/g) having a mean particle diameter of 0.1 μm , 220 g of V_2O_5 and 120 g of calcium dodecylbenzenesulfonate were suspended in 885 ml of deionized water and stirred for 18 hours to achieve homogeneous dispersion. The solids content of the suspension obtained was 50% by weight. 60 g of organic binder, namely a copolymer of vinyl acetate and vinyl laurate, in the form of a 50% strength by weight aqueous dispersion were then added. Using this coating suspension, a monolithic ceramic support honeycomb made of cordierite and having a cell density of 200 cpsi and dimensions of 7.5 cm \times 7.5 cm \times 15 cm was coated using a method analogous to Example 15. Due to the viscosity-lowering action of the surfactant, the suspension not adhering to the wall flowed completely out of the channels without problems. Owing to the high solids content of the suspension used, 108 g of active composition per liter of catalyst could be applied in a single coating step. No channels of the honeycomb were blocked with active composition.

Example 18 (Catalyst 3 according to the invention):

To produce a catalyst based on a TiO_2 having a larger mean particle diameter, 785 g of TiO_2 (BET about 30 m^2/g) having a mean particle diameter of 0.4 μm , 196 g of V_2O_5 and 46 g of alkyl(C_8 - C_{10})polyoxyethylene ether phosphate were suspended in 910 ml of deionized water and stirred for 18 hours to achieve homogeneous

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dispersion. The solids content of the suspension obtained was 52% by weight. 60 g of organic binder, namely a copolymer of vinyl acetate and vinyl laurate, in the form of a 50% strength by weight aqueous dispersion were then added. Using this coating suspension, a monolithic ceramic support honeycomb made of cordierite and having a cell density of 200 cpsi and dimensions of 7.5 cm x 7.5 cm x 15 cm was coated using a method analogous to Example 15. Due to the viscosity-lowering action of the surfactant, the suspension not adhering to the wall flowed completely out of the channels without problems. Owing to the high solids content of the suspension used, 97 g of active composition per liter of catalyst could be applied in a single coating step. No channels of the honeycomb were blocked with active composition.

Example 19 (Oxidation of o-xylene/air mixtures having a low o-xylene concentration):

To examine the catalytic properties, the catalysts were tested for suitability in (by way of example) the oxidation of o-xylene and compared to a conventional catalyst produced according to the prior art (ring-shaped catalysts). The test apparatus used comprised an adiabatic, i.e. uncooled, insulated reactor. The reactor was constructed so that it could be charged both with catalyst rings and with a honeycomb catalyst according to the invention. An air preheater by means of which the o-xylene/air mixture could be heated to 300-360°C was installed upstream of the reactor. The cross-sectional inflow area of the catalyst was 19.6 cm² and the catalyst fill height was 10.2 cm. The experiments were carried out at a space velocity of 20,000 h⁻¹. The concentration of o-xylene in the gas mixture at the reactor inlet was in the range from 500 to 600 mg/standard m³. The o-xylene concentration was measured by means of gas chromatography and also an on-line FID detector. The

The catalysts from Comparative Example 13 and from Example 16, and also a ring-shaped catalyst (Example 15) as further comparison, were tested using 10 the above-described apparatus. The active compositions of all three catalysts had the same chemical composition.

The test results are summarized in Table 1 below.

Table 1: Catalyst tests using low-concentration o-xylene/air mixtures

	Comparative catalyst on rings (Example 15)	Honeycomb catalyst with 20 g of active composition/l of catalyst (Example 13)	Honeycomb catalyst according to the invention with 112 g of active composition/l of catalyst (Example 16)
Temperature at gas inlet	340°C	340°C	340°C
o-xylene conversion /mol%	56	82	95
PA selectivity/mol%	41	62	67
O-tolualdehyde/mg/Standard m ³	22	42	12
Phthalide mg/Standard m ³	20	36	14

5 **Example 20 (Suitability of the monolithic catalysts produced according to the invention for (by way of example) the after-reaction of PA process gas from o-xylene oxidation in a post-reactor):**

10 The test apparatus used (post-reactor) comprised an adiabatically operated (well insulated) reaction tube in which the monolithic catalyst of the invention from Example 18 was installed. The post-reactor was installed downstream of a customary PA pilot reactor (main reactor). The gas line between main reactor and post-reactor could be thermostatted so that
 15 variable gas inlet temperatures into the post-reactor were possible. Gas sampling points were installed before the inlet and at the outlet of the post-reactor. Furthermore, the reaction gas could be cooled in a condenser (desublimator) either after leaving the main
 20 reactor or after leaving the post-reactor and the PA

formed could be deposited or isolated. The main PA reactor was 3.3 m long and had a tube diameter of 25 mm. The temperature of the reactor was regulated using a circulated salt bath (eutectic melt of potassium nitrate and sodium nitrite). The amount of air fed in was always 4 standard m³/h. The main PA reactor was charged with a commercial PA catalyst and the catalyst fill height was 2.8 m. The salt bath temperatures were selected so that the gas mixture leaving the reactor still had comparatively high contents of unreacted o-xylene and underoxidation products such as phthalide and tolualdehyde. The o-xylene loading upstream of the reactor was constant at 70 g/Standard m³ of gas during the experiments. The air/o-xylene mixture was preheated to 180°C before entering the main reactor.

The reaction gas leaving the main reactor was brought to the desired temperature by means of thermostating and passed through the post-reactor containing the monolithic catalyst. The amount of monolithic catalyst was selected so that a space velocity of 20,000 h⁻¹ resulted.

The reaction gas leaving the post-reactor was subsequently passed through a desublimator in order to deposit the reaction products PA, phthalide, etc.

In order to be able to assess the efficiency of the post-reactor in respect of degradation or further oxidation of the by-products, part of the PA reaction gas both before and after the post-reactor was analyzed by scrubbing the gas in acetone and subsequently determining the o-xylene, phthalide and tolualdehyde contents by gas chromatography. The CO and CO₂ contents in the reaction gas before and after the post-reactor were measured by IR spectroscopy. The PA yield was, as already mentioned, determined by means of deposition in a desublimator or calculated via a mass balance.

The results of the experiments are shown in Table 2 below.

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Table 2: Results of the oxidation experiments on PA reaction gas

	Contents* before/without post-reactor	Contents* in % by weight after post-reactor with catalyst from Ex. 18 at various gas inlet temperatures			
		360°C	340°C	320°C	300°C
Phthalide	0.48% by weight	0.005	0.014	0.041	0.101
o-Xylene	0.25% by weight	0	0.004	0.022	0.081
p-Benzoquinone	0.04% by weight	0.012	0.015	0.019	0.022
o-Tolualdehyde	0.21% by weight	0	0.004	0.011	0.026
PA yield	111.0% by weight	111.3	111.5	111.8	112.2

* Based on the total organic constituents in the reaction gas.

The results in Table 2 show that a major part of the underoxidation products can be removed from the reaction gas and oxidized further to PA by using the monolithic catalysts of the invention in a downstream adiabatic reactor (post-reactor) in the PA process. Surprisingly, this also takes place at relatively high space velocities. To achieve the best yield, the after-reaction is advantageously carried out at low gas inlet temperatures. The optimum reaction conditions are a compromise between yield and amount of by-products.

Example 21: (Suitability of the monolithic catalysts produced according to the invention for (by way of example) the after-reaction of PA process gas from naphthalene oxidation in a post-reactor):

The experiment was carried out using a method analogous to Example 20, except that the main reactor was charged with a commercial PA catalyst suitable for naphthalene oxidation and was supplied with a naphthalene/air mixture. The monolithic catalyst of the invention from Example 18 was installed in the post-reactor. In this example too, the salt bath temperature

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in the main reactor was selected so that the gas mixture leaving the reactor still had comparatively high contents of unreacted naphthalene and the by-product naphthoquinone. The naphthalene loading of the feed to the main reactor was a constant 70 g/Standard m³ at 4 standard m³ of gas/h during the experiment.

The results of the experiment are shown in Table 3 below.

10

Table 3: Results of the oxidation experiments on PA reaction gas from naphthalene oxidation

	Contents* before/without post-reactor	Contents* after post- reactor with catalyst from Ex. 18 at a gas inlet temperature of 350°C
Naphthalene.	0.12% by weight	0.02% by weight
Naphthoquinone	0.54% by weight	0.06% by weight
PA yield	99.7% by weight	100.3% by weight

* Based on the total organic constituents in the reaction gas.

15

The results in Table 3 show that, in the PA process using naphthalene as feed, a major part of the residual naphthalene and the by-product naphthoquinone can be removed from the reaction gas and oxidized further to PA by using the monolithic catalysts of the invention in a downstream adiabatic reactor (post-reactor).

20

Claims:

1. A process for producing monolithic supported catalysts for gas-phase oxidation by coating the catalyst support by means of a suspension, wherein the latter comprises catalytically active composition and one or more surfactants of the formula



where R is the hydrophobic part(s) of the surfactant and n is 1, 2 or 3; Y is the hydrophilic part of the surfactant and m is 0, 1, 2 or 3, and X is the hydrophilic head group of the surfactant.

2. The process as claimed in claim 1, wherein the surfactant content is from 1 to 10% by weight.

3. The process as claimed in claim 1 or 2, wherein the head groups X present in the surfactants are functional groups selected from among carboxylates, polycarboxylates, phosphates, phosphonates, sulfates and sulfonates.

4. The process as claimed in claim 3, wherein all or some of the functional groups of the head group X are present as free acid groups, ammonium salts or alkaline earth metal salts.

5. The process as claimed in any of claims 1 to 4, wherein the hydrophilic group Y is bound to the central atom of the head group X either directly or via an oxygen.

6. The process as claimed in any of claims 1 to 5, wherein the hydrophobic groups R of the surfactants used are bound to the head group via a hydrophilic group Y.

7. The process as claimed in any of claims 1 to 6, wherein the hydrophobic parts R of the surfactants used are saturated, unsaturated or branched alkyl radicals with carbon building blocks having from 5 to 30 carbon atoms and are bound either directly or via aryl groups to the hydrophilic part Y or the head group X.

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8. The process as claimed in any of claims 1 to 7, wherein the hydrophilic radicals Y of the surfactants used comprise polymeric alkoxy units whose degree of polymerization is from 1 to 50 monomer units.

9. The process as claimed in any of claims 1 to 8, wherein one or more surfactants selected from the group consisting of calcium alkylarylsulfonates, alkylphenol ethoxylates, ammonium alkylarylsulfonates, calcium dodecylbenzenesulfonate, polyethoxy(dinonyl phenyl ether phosphate), polyoxoethylene(lauryl ether phosphate), polyethoxy(tridecyl ether phosphate), calcium dodecylbenzenesulfonate, tridecyl phosphate esters, ethoxylated phosphated alcohols, alkyl polyoxyethylene ether phosphate, ammonium nonyl phenyl ether sulfate, are used.

10. The process as claimed in any of claims 1 to 9, wherein the catalytically active composition is produced from one or more types of TiO_2 .

11. The process as claimed in claim 10, wherein the catalytically active composition further comprises V_2O_5 as additional component.

12. The process as claimed in claim 10 or 11, wherein the catalytically active composition comprises promoters.

13. The process as claimed in any of claims 1 to 12, wherein the catalyst supports used are one or more materials selected from the group consisting of cordierite, silicates, silicon dioxide, silicon carbide, aluminum oxide, aluminates, metals or metal alloys.

14. The process as claimed in any of claims 1 to 13, wherein the catalyst support bodies used are honeycombs or supports having open and/or closed cross-channel structures.

15. The process as claimed in claim 14, wherein the catalyst support bodies used are honeycombs having a cell density, i.e. a number of channels, of from 100 to 400 csi (cells per square inch).

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16. The use of a monolithic supported catalyst obtainable by the process as claimed in any of claims 1 to 15 in an adiabatic reactor in combination with an isothermally operated reactor for preparing phthalic anhydride from o-xylene.

17. The use of a monolithic supported catalyst obtainable by the process as claimed in any of claims 1 to 15 in an adiabatic reactor in combination with an isothermally operated reactor for preparing phthalic anhydride from naphthalene.

18. The use of a monolithic supported catalyst obtainable by the process as claimed in any of claims 1 to 15 in an adiabatic reactor in combination with an isothermally operated reactor for preparing phthalic anhydride from o-xylene/naphthalene mixtures.

19. The use of a monolithic supported catalyst as claimed in any of claims 16 to 18 in an adiabatic reactor having upstream gas cooling in combination with an isothermally operated reactor.

20. The use of a monolithic supported catalyst as claimed in any of claims 16 to 19 in an adiabatic reactor having upstream gas cooling, where gas cooling and the reaction are carried out in a joint apparatus, in combination with an isothermally operated reactor.

21. The use of a monolithic supported catalyst as claimed in any of claims 16 to 20 in an adiabatic reactor having upstream gas cooling and downstream gas cooling, where gas cooling and the reaction are carried out in a joint apparatus, in combination with an isothermally operated reactor.

22. A catalyst obtainable by coating the catalyst support by means of a suspension, wherein the latter comprises catalytically active composition and one or more surfactants of the formula



where R is the hydrophobic part(s) of the surfactant and n is 1, 2 or 3; Y is the hydrophilic part of the

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Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen

(54) Title: METHOD OF PRODUCING MONOLITHIC OXIDATION CATALYSTS AND THEIR USE IN GAS PHASE OXIDATION OF CARBOHYDRATES

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON MONOLITHISCHEN OXIDATIONSKATALYSATOREN UND DEREN VERWENDUNG BEI DER GASPHASENOXIDATION VON KOHLENWASSERSTOFFEN

(57) Abstract: The invention relates to a method of producing monolithic substrate catalysts and to their use in the gas phase oxidation of carbohydrates. Said catalysts are obtained by coating the catalyst substrate with a suspension that consists of a catalytically active compound and one or more surfactants of the general formula R_nY_mX . R represents the hydrophobic part of the surfactant, with n being 1, 2 or 3. Y represents the hydrophilic part of the surfactant, with m being 0, 1, 2 or 3 and X represents the hydrophilic head group of the surfactant.

(57) Zusammenfassung: Die Erfindung betrifft ein Verfahren zur Herstellung und die Verwendung von monolithischen Trägerkatalysatoren für die Gasphasenoxidation durch Beschichtung des Katalysatorträgers mit einer Suspension die aus katalytisch aktiver Masse und einem oder mehreren Tensiden der allgemeinen Formel R_nY_mX besteht. R steht dabei für den hydrophoben Teil des Tensides mit n gleich 1, 2 oder 3; Y für den hydrophilen Teil des Tensides mit m gleich 0, 1, 2 oder 3 und X für die hydrophile Kopfgruppe des Tensides.

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As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

PROCESS FOR PRODUCING MONOLITHIC OXIDATION CATALYSTS AND THEIR USE
IN THE GAS-PHASE OXIDATION OF HYDROCARBONS

the specification of which (check only one item below):

- ☐ is attached hereto.
- ☐ was filed as United States application
Serial No. _____
on _____
and was amended
on _____ (if applicable).
- ☒ was filed as PCT international application
Number PCT/EP00/05519
on June 15, 2000
and was amended under PCT Article 19
on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
Germany	199 31 902.2	8 July 1999	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

U.S. APPLICATIONS			STATUS (Check One)		
U.S. APPLICATION NUMBER	U.S. FILING DATE		PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)			

POWER OF ATTORNEY As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration numbers):

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 101	SIGNATURE OF INVENTOR 102	SIGNATURE OF INVENTOR 103
<i>[Signature]</i>	<i>[Signature]</i>	<i>[Signature]</i>
DATE	DATE	DATE
3. Dec. 2001	4.12.01	14.1.02

10030514 150302

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7	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY STATE & ZIP CODE/COUNTRY
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME SECOND GIVEN NAME
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2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME SECOND GIVEN NAME
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY COUNTRY OF CITIZENSHIP
9	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY STATE & ZIP CODE/COUNTRY

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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DATE 5.12.2001	DATE 17.12.01	DATE 21.12.2001
SIGNATURE OF INVENTOR 207	SIGNATURE OF INVENTOR 208	SIGNATURE OF INVENTOR 209
DATE	DATE	DATE